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RESEARCH PAPER

Preparation and properties of biodegradable bamboo powder/ poly-caprolactone composites

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Abstrat: The bamboo powder/polycaprolactone composites (BPPC) were prepared by torque-rheometer to investigate the effects of recipes and processing conditions on the rheological properties of BPPC. The morphological behavior and mechanical properties of BPPC were also studied. Results showed that the optimum recipe for composite materials is composed of 70% of polycaprolactone, 30% of bamboo powder according to volume, 1.6 % of aluminate coupling agent, 1.2% of stearic acid, and 2% of paraffin to bamboo powder according to mass ratio. The optimum processing condition parameters were determined as the rotational speed at 50 r·min^{-1} and the temperature at 100ºC for BPPC. The BPPC (containing 30 copies bamboo powder) possessed eminent interfacial compatibility and mechanical properties of BPPC.

Keywords: bamboo powder; polycaprolactone; rheological properties; mechanical properties

Introduction

With the increasing use of plastic product, the pollution from waste plastics has become more and more serious problems. This fact leads to the use of eco-friendly biocomposites derived from bio-fibers and biodegradable polymers which not only can decrease the plastic pollution but also can reduce the widespread dependence on fossil resources (Mohanty et al. 2000). Polycaprolactone (PCL) has been used one of the most versatile and commercially available biodegradable polymers, because its properties such as low density, biodegradability, compostability and compatibility with different forms of waste disposal, are very similar to those of low density polyethylene (Hülya et al. 2003; Jiménez et al. 2007). However, PCL has a drawback of high cost and its funcation is restricted in potential applications. In order to reduce its cost, polycaprolactone has been successfully blended with natural polymers, which has the characteristics such as large amount of resouce, low cost, high modulus and high aspect ratio, including chitosan (Yang et al. 2001) and starch (Mani 2001; Bastioli 1998; Vert 1992; Saha et al. 1989). Among many natural fibrous plants, bamboo is one of the fastest growing grassplants and it is abundantly available in many countries. Unfortunately, in spite of its remarkable tensile and impact strength (Ray et al. 2004), bamboo has been utilized only for making low grade structural materials so far. Conventional processing methods, such as extrusion/calendering are suitable for PCL, because PCL possesses charateristics of low melting temperature and crystallization temperature. Torque rheometers are used in labroratory-scaled test and have been also widely used in processing industries for many years. With this regard, in the present study, we mainly analyzed the effect of formulation and poccessing conditions on rheological properties and determined the mechanical properties and morphological behavior of bamboo powder/polycaprolactone composites (BPPC).

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Materials and methods

Bamboo powder (BP) passing 80 meshs was kindly supplied by Yongan Forestry (China). Polycaprolactone (PCL, Placcel H7-FG-212) was from Daicel Chemical Industries, Ltd. (Japan). Aluminate coupling agent was supplied by Polymer Factory, Fujian Normal University. Stearic acid (SA) and Paraffin (56-58) were purchased from market.

Bamboo powder was prestirred for 2 min before mixing with additives in high-speed disintegrating machine (JFW-A, China) at the rotational speed of 2600 r·min^{-1}. Aluminate coupling agent, stearic acid and paraffin were put into the high-speed disintegrating machine every 2 min in turn in order to react with bamboo powder completely. The measurements rheological proper-

ties were carried out by using Polylab Rheomix 600 OS (HAAKE, Germany) coupled to Roller-Rotors R600. The sheets of BPPC in different mass proportions were prepared in a twin-screw extruder of Polylab Rheomix PTW24/28 at 90–110ºC and at a screw rotational rate of 100 r·min^{-1}. The mechanical properties were evaluated by a universal testing machine (LR5K) at a crosshead speed of 5 cm·min^{-1} (according to ASTM D412. The sheets of BPPC were cut into several portions by a punch with dumbbell-shaped die. Five portions of the specimen were tested and the mean data were reported. The brittle fracture surfaces of impact specimens were observed by a JEOL scanning electron microscope (SEM), Model JSM-6380LV. The scanned surfaces were coated with a gold layer to avoid charging under the electron beam.

Results and discussion

Rheological properties

The melting torque values decreased rapidly from 63 Nm in the first minute and dropped afterwards to a steady value of 16 Nm in the absence of aluminate coupling agent (Fig. 1). However, when a little coupling agent (0.8%–1.6%) was added to bamboo powder, the values of melting torque decreased. When the coupling agent increased to 2.4%, the loading peak value (all the sample is fed into the mixer) decreased rapidly from 63 Nm to 47 Nm (Fig. 1(b)). On the other hand, the melting torque value only decreased to 21 Nm before it increased to a higher final value of 23 Nm (Fig. 1(a)). The loading peak changed less and the values of melt torque and plastic torque were higher if the coupling agent was increased further to 3.2%. This may be due to the chemical reaction between the hydroxyl groups of the bamboo powder and carbonyl groups of the coupling agent (Chen et al. 2009) during the blending process. However, the amount of coupling agent in the mixed phase also plays an important role in compatibility to a great extent, because the coupling agent can reduce interfacial tension and the tendency of the dispersed particles to coalesce. The adverse effect of excess coupling agent on the dispersion of the bamboo powder in the polycaprolactone matrix may be attributed to reactions within the functional groups in aluminate's coupling agent (Joshi et al. 2006), which would not improve the compatibility between the blended polymers. The torque values at 1.5 min increased during the reactive blending process for blends containing coupling agent. The coupling agent of 1.6% was used in the preparation of BPPC in order to increase interfacial connection and decrease energy cost.

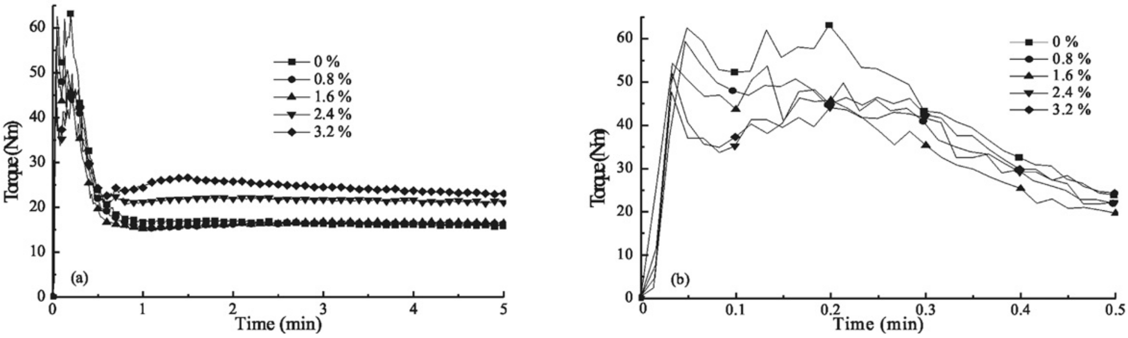

Fig. 1 Effect of coupling agent contents on rheological properties

(a)----effect of coupling agent contents on torque; (b)----the partial enlarge drawing of Fig.1 (a)

The inner lubricant of stearic acid had little effect on the blends of bamboo powder and PCL at first (Fig. 2). However, when the ratio of stearic acid to bamboo powder increased from 0.8% to 1.2% in bamboo powder/PCL blends, the torque value decreased to a lower value. On the contrary, the result of the excess stearic acid (1.6%) showed that the torque-time curves move upwardly, compared with 1.2 % of stearic acid (Joshi et al. 2006). As shown in Fig. 2(b), when 1.2% of stearic acid was increased in composite, the torque value was the lowest and the processing energy cost effectively decreased.

Lubricants such as paraffin can be used to decrease the instrument wastage when the materials are fed and homogenized in the extruder at practical process. As shown in Table 1, in the absence of paraffin, the value of loading peak reached 121 Nm and the material temperature at the same time increased to 126.9ºC within 5 min. Therefore, PCL was blended with bamboo powder at mixer chamber, the instrument wastage was very large without lubricant. It was difficult to clear BPPC away from the rollers and mixer chamber because of the high viscosity of composites when lacking lubricant. The torque value of loading peak decreased rapidly when paraffin was 1%. When the amount of paraffin increased to 2%, the torque value of loading peak and the balanced torque decreased largely and the final temperature of blends can not exceed 115ºC., the amount of torque value was reduced to 41.5 Nm while the amount of paraffin was up to 3%. It was indicated that excess lubricant was not available because the polycaprolactone interface was difficult to be broken.

It is better to use the higher processing temperature in theory, because higher processing temperature was beneficial not only for improving the fluid of the blends, but also for decreasing balance viscosity and energy cost. However, the most important drawback of PCL is the sensitivity to temperature (Jiménez 2006) and its upper limit temperature is only 120ºC. When the blends were mixed at 120ºC, the material temperature had reached 137.2ºC in 5 min, which had exceed the upper limit processing temperature of the PCL (Table 2). Therefore, the optimum proc-

essing temperature is 100ºC for avoiding degradation of PCL.

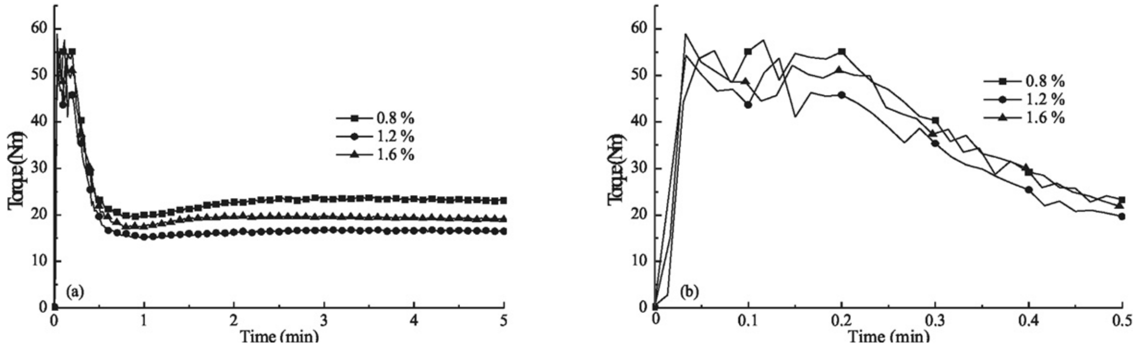

Fig. 2 Effect of stearic acid contents on rheological properties

(a)----effect of stearic acid contents on torque; (b)----the partial enlarge drawing of figure (a)

Table 1. Effect of paraffin on rheological properties

Paraffin (%)	Torque of loading peak (Nm)	Balanced torque (Nm)	Material temperature in 5 min (ºC)	Energy cost (kJ)
0	120.7	24.9	126.9	52.82
1	81.2	24.4	125.9	48.43
2	53.7	17.8	115	32.57
3	41.5	9.6	108.1	20.06

Table 2. Effect of processing temperatures on rheological properties

Processing temperature (ºC)	Material temperature in 5 min (ºC)	Degraded time (min)	Blanced torque (Nm)	Energy cost (kJ)
90	111.9	>5	25.7	42.03
100	119.3	>5	23.6	40.19
110	127.6	2.21	21.9	38.38
120	137.2	1.30	21.1	37.68

The effect of rotational speed on the rheological properties was less than that of processing temperature (Table 3). The higher sheer rate could break the resin interface more effectively, as led to earlier and narrower plastic peak. The higher sheer rate induced the more energy cost. At the same time, high sheer rate also resulted in the rapid increase of material temperature. For example, the temperature of blends reached 125ºC in 5 min at the rotational speed of 60 r·min^{-1}. The temperature of the blends was under 120ºC when the rotational speed was 50 r·min^{-1}. Therefore, it was appropriate to select the rotational speed of 50 r·min^{-1} in order to avoid overhigh material temperature.

Table 3. Effect of rotational speeds on rheological properties

Rotational speed （r·min^{-1}）	Material temperature in 5 min （ºC）	Time of plastic peak (min)	Half-peak width of plastic peak (min)	Blanced torque （Nm）	Energy cost （kJ）
40	114.2	1.31	0.66	22.7	32.33
50	119.3	1.11	0.59	23.6	40.19
60	125.1	0.88	0.49	35.4	49.23

When bamboo powder contents increased from 10% to 30% (mass ratio of the total value of BP to PCL), loading peak became broader (Table 4). Once the amount of bamboo powder increased to 50%, the loading peak changed higher and broader and the plastic peak almost disappeared (Table 4).

Table 4. Effect of the contents of bamboo powder on rheological properties

Mass ratio of BP to PCL	Torque of loading peak (Nm)	Half-peak width of loading peak (min)	Torque of plastic peak (Nm)	Blanced torque (Nm)
10:90	56.3	0.05	10.5	21
30:70	56.2	0.21	6.3	22
50:50	71.5	0.23	1.1	14.2

Mechanical properties

The results of mechanical properties of BPPC in different mass proportions showed that elongation value and tensile strength of composites decreased with the increase of bamboo powder content (Fig. 3). For irregular shape fillers, the strength of the composites decreases due to the inability of the filler to support stresses transferred in the polymer matrix. However, the samples containing 30% bamboo powder (mass ratio of the total value of BP to PCL) could still transfer stresses in the matrix effectively, so they could maintain an elongation value of 545% and a tensile strength value of 18 MPa.

Morphological behavior

SEM micrograph of the brittle fracture surface of BPPC showed that the crosslinking reactions between bamboo powder and PCL increased their compatibility at the presence of coupling agent (Fig. 4). The fracture surface became very smooth due to the action of hydrogen bonds between the hydroxyl groups of bamboo powder and the carbonyl groups of PCL at the presence of coupling agent when the amount of bamboo powder was 10% (mass ratio of BP to the total of BP and PCL). However, when the content of bamboo powder increased to 30%, some bamboo fibres uncoated coupling agent were pull out completely and left

some cavities in the polycaprolactone matrix. This may be due to the existence of a great deal of bamboo powder affecting the compatibility achieved. When amount of bamboo powder was 50%, BPPC compatibility was affected at greater extent than 30% BP.

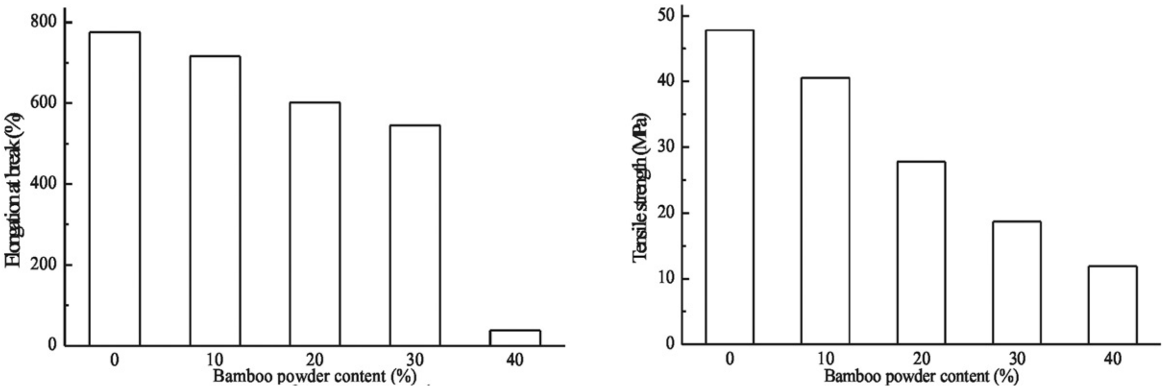

Fig. 3 Effect of bamboo powder contents on elongation value at different break and tensile strengths

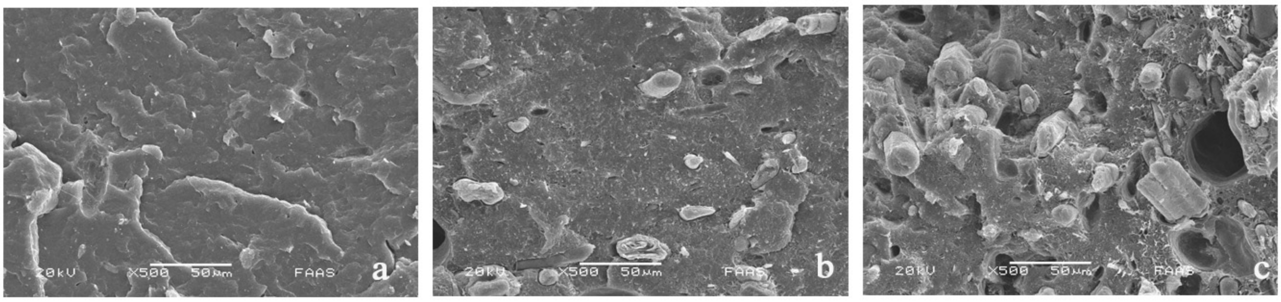

Fig. 4 SEM images of brittle fracture surface（bamboo powder content in the total value of BP and PCL） a is 10%; b is 30%; c is 50%.

Conclusions

Rheological measurement can provide the following parameters: the curves of torque, material temperature and energy cost vs time synchronously at the course of polymer processing. The possible reactions of materials, such as crosslinking, grafting and degradation and so on, can be evaluated from torque-time curve. The preparation of BPPC should be to avoid the degradation of PCL, overhigh material temperature and big energy cost. Aluminate coupling agent of 1.6% increased the compatibility of bamboo powder and polycaprolactone. The energy cost was decreased at the present of lubricant because 1.2% of stearic acid and 2% of paraffin decreased the attrition between the sample and the screw with the extruder. It was best to prepare BPPC at the temperature of 100ºC and at the rotational speed of 50 r·min^{-1} for avoiding the thermodegradation of PCL. The mass ratio of BP to PCL should be less than 30:70 in order to get the eminent interfacial compatibility and mechanical properties during composites machining processes.

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